STUDIES ON THE STABILITY OF THE DIMER OF 2,4-TOLYLENE DIISOCYANATE

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ABSTRACT

A series of carbamates of the dimer of 2,4-tolylene diisocyanate was prepared from different alcohols, leaving the uretidine-dione ring unaffected. Di-*sec*-butylamine and dibenzylamine did not affect the dimer ring and reacted only with the two free isocyanate groups. However, di-*n*-propylamine, di-*n*-butylamine, and di-*n*-amylamine ruptured the ring, and diureas of the monomer were obtained. Alkaline reduction changed the dimer ring into a ureylene link and a N-substituted amide was formed by the Leuckart reaction. Hydrazine hydrate gave an unsymmetrical monosubstituted urea whereas hydroxylamine broke the ring and gave the corresponding oxime of the formamide.

INTRODUCTION

In the manufacture of polyurethanes, polymeric diols are chain-extended with diisocyanates such as 2,4-tolylene diisocyanate (TDI) (1). Since commercial TDI contains a dimer it is of interest to study the stability of the uretidine-dione ring of the dimer (TDID), which shows isocyanate activity at relatively higher temperatures than the monomer. This property is being used to modify elastomers, plastics, and foams (2).

RESULTS

When the dimer of 2,4-tolylene diisocyanate was reacted with alcohols at about 90°, the corresponding diurethanes were formed, giving only traces of allophanates. The diurethanes prepared are listed in Table I. Higher temperatures in the range of 125 to 160° and catalysts such as triethylamine and N-methyl morpholine appeared to be necessary for the formation of allophanates (3) and triphenyl isocyanates (4).

TDID did not react with the *tert*-butyl alcohol probably because of its easy dehydration. Benzyl alcohol gave a reaction product which analyzed for a compound made from 1 mole of TDI and 2 moles of benzoic acid. However, this compound could not be prepared from TDI and benzoic acid. Under milder conditions only 1 mole of benzoic acid reacted with the isocyanate group in para position, which was due to the high reactivity of the para group compared to the ortho group (5).

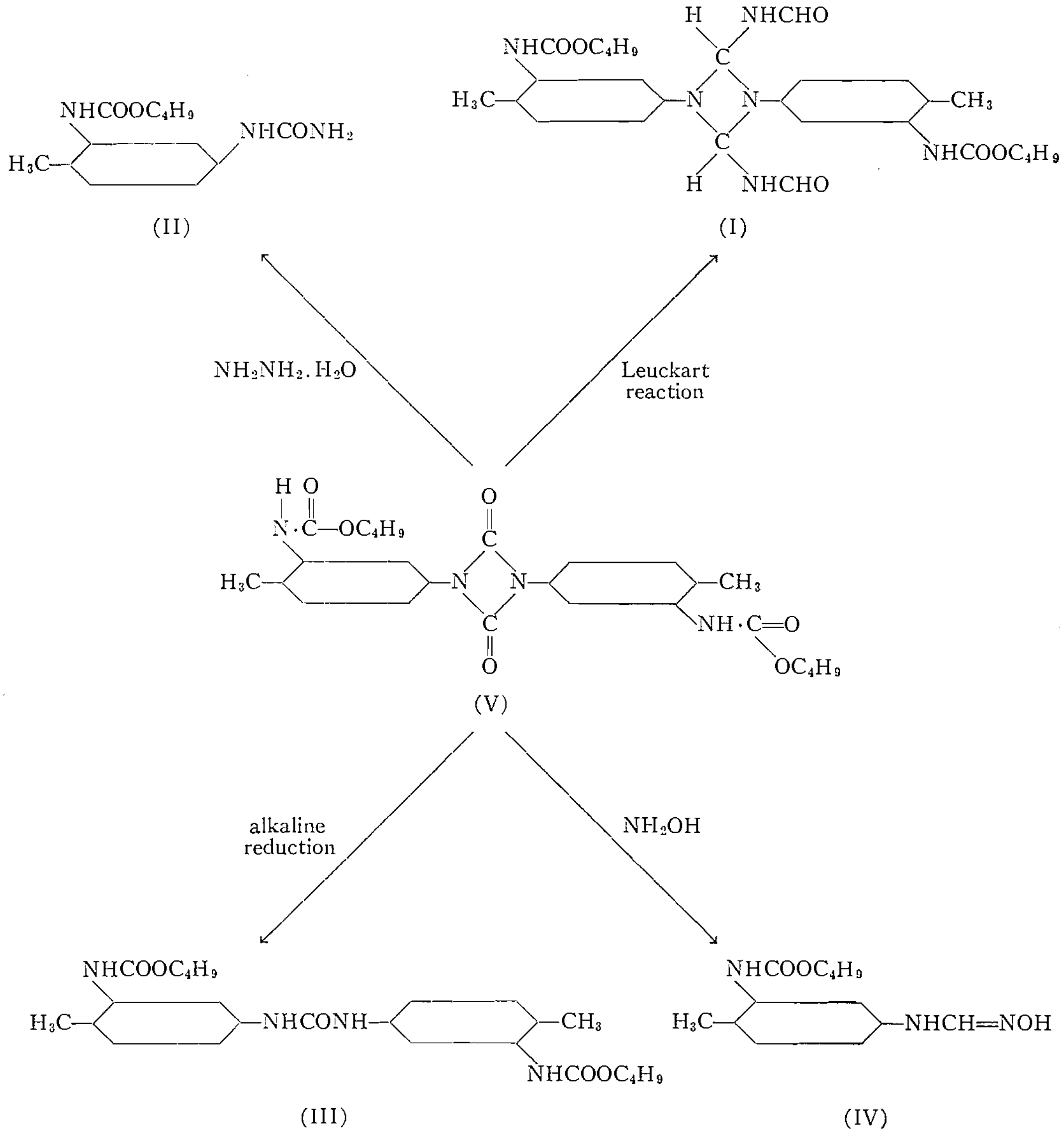
The failure to dimerize 3-methylcarbamyl-2-isocyanatotoluene in pyridine was probably due to the fact that the *o*-isocyanate is hindered (6). Heating under reflux with benzene or ethyl acetate in excess changed TDID to an amorphous powder which was insoluble in all common organic solvents, but soluble in dimethylformamide. On heating the product to 215° for 45 minutes a yellow, hard-setting resin was obtained which was soluble in dimethylformamide.

Some of the dialkylamines used, such as di-*n*-propyl, di-*n*-butyl, and di-*n*-amylamines, ruptured the uretidine-dione rings of TDID very easily (Table II). In *o*-dichlorobenzene, the dimer ring was found to react with di-*n*-butylamine at an appreciable rate even at

TABLE I

1,3-Bis(4′-methyl-3′-R-carbamylphenyl) uretidine-2,4-dione

R	Yield (%)	M.p. (°C)	Crystallization solvent	Reflux time (hr)	Formula	C Calc. (%)	C Found (%)	H Calc. (%)	H Found (%)
Methyl	90	207–208	$HCON(CH_3)_2$	3	$C_{20}H_{20}O_6N_4$	58.2	58.3	4.85	4.92
Ethyl	95	205	Dioxane	4	$C_{22}H_{24}O_6N_4$	60.0	59.9	5.46	5.46
n-Propyl	85	197	$HCON(CH_3)_2$	3	$C_{24}H_{28}O_6N_4$	61.5	61.4	6.00	5.91
Isopropyl	84	215	"	3	$C_{24}H_{28}O_6N_4$	61.5	61.9	6.00	6.27
n-Butyl	98	197.5	Cellosolve	4	$C_{26}H_{32}O_6N_4$	62.9	62.9	6.45	6.54
Isobutyl	98	205	"	3	$C_{26}H_{32}O_6N_4$	62.9	63.3	6.45	6.57
n-Amyl	90	197	"	4	$C_{28}H_{36}O_6N_4$	64.1	63.7	6.87	6.72
Isoamyl	87	199	$HCON(CH_3)_2$	3	$C_{28}H_{36}O_6N_4$	64.1	63.9	6.87	7.10
3-Pentyl	90	198	Cellosolve	3	$C_{28}H_{36}O_6N_4$	64.1	63.5	6.87	6.77
n-Hexyl	80	186	$HCON(CH_3)_2$	3	$C_{30}H_{40}O_6N_4$	65.2	65.0	7.24	7.24
n-Heptyl	99	185	"	4	$C_{32}H_{44}O_6N_4$	66.2	65.8	7.65	7.77
n-Octyl	98	185	"	4½	$C_{34}H_{48}O_6N_4$	67.1	67.1	8.00	7.99
Capryl	98	186	"	5	$C_{34}H_{48}O_6N_4$	67.1	67.5	8.00	8.56
n-Dodecyl	70	180 (softens at 170)	Benzene and dioxane	5	$C_{42}H_{64}O_6N_4$	70.0	69.9	8.88	8.82



50° (7, 8). Diisobutylamine and dibenzylamine, however, left the ring unaffected and reacted with the *o*-isocyanate groups to yield substituted ureas (Table III). Both compounds showed characteristic infrared absorption bands for CO stretching frequency of the four-membered uretidine-dione ring.

For the oxidation, reduction, and carbonyl activity studies the two free isocyanate groups in TDID were blocked by forming the *n*-butyl urethanes (V). The structure of the new diurethane derivative of TDID was derived from its analysis and infrared spectrum. The blocking of the two isocyanate groups seemed to enhance the stability of the uretidine-dione ring. Heating a solution of the compound in benzene or ethyl acetate under reflux did not affect the ring, which was found to be moderately stable toward oxidation by potassium persulphate, lead tetraacetate, and selenium dioxide in dioxane.

TABLE II

2,4-Bis(N′,N′-di-R-ureido) toluene

R	Yield (%)	M.p. (°C)	Crystallization solvent	Reflux time (hr)	Formula	C Calc. (%)	C Found (%)	H Calc. (%)	H Found (%)
Di-*n*-propyl	60	124	Pet. ether	4$\frac{1}{2}$	$C_{21}H_{36}O_2N_4$	67.0	67.0	9.57	9.63
Di-*n*-butyl	80	111	"	4	$C_{25}H_{44}O_2N_4$	69.4	69.4	10.18	9.88
Di-*n*-amyl	50	98	"	3	$C_{29}H_{52}O_2N_4$	71.3	71.7	10.66	10.70

TABLE III

1,3-Bis(4′-methyl-3′-(N′,N′-di-R-ureido)phenyl) uretidine-2,4-dione

R	Yield (%)	M.p. (°C)	Crystallization solvent	Reflux time (hr)	Formula	C Calc. (%)	C Found (%)	H Calc. (%)	H Found (%)
Di-*sec*-butyl	70	176	Dioxane	3	$C_{34}H_{50}O_4N_6$	67.3	66.8	8.38	8.32
Di-benzyl	80	197	$HCON(CH_3)_2$	9$\frac{1}{2}$	$C_{46}H_{42}O_4N_6$	74.4	74.6	5.66	6.16

Alkaline reduction by various reagents such as sodium methylate, magnesium methylate, ammonium sulphide, or zinc and alcoholic ammonia all readily changed the ring into the ureylene link, with the appearance of CO and NH absorption bands at 1630 and 1602 cm^{-1} respectively. In alkaline medium, it seems that the ring was dissociated and that one of the isocyanate groups was hydrolyzed to amino group, which in turn reacted with the other isocyanate group to give symmetrical ureas. Hydrazine hydrate, on the other hand, reduced the ring to form an unsymmetrical monosubstituted urea.

The Leuckart reaction seems to give the corresponding N,N-substituted amide, according to infrared spectra determination. The new absorption for CO stretching (formyl group) at 1662 cm^{-1} (m) coupled with the appearance of free NH stretching vibration at 3410 cm^{-1} (m) and 3010 cm^{-1} (w) provide evidence for the presence of formyl derivatives of the primary amine (9). The failure to isolate any carbamate from the alcoholic solvent further lent credence to the conclusion that the uretidine-dione ring was intact. There was evidence that the CO group in the uretidine-dione ring acted as a true carbonyl, since hydroxylamine gave the oxime in poor yield. The elemental analysis corresponded to that of a N-substituted formamide oxime obtained from the monomer. This was also supported by the appearance of C—N and N—OH absorption bands and the absence of —N=C=N— absorption bands.

EXPERIMENTAL

General

The reactions with alcohols and diamine were performed in a 100-ml three-necked flask fitted with a mercury sealed stirrer. The condenser carried a $CaCl_2$ tube. Alcohols and diamines were taken in excess (2–3 ml) for 0.001 mole (1.0 g) of the dimer. The solvent used for the reactions was petroleum ether, A.R. (B.D.H.), b.p. 80–100° (40 ml). After the reaction was over the mixture was cooled, the compound filtered, washed, and dried in vacuum before crystallization.

All the melting points reported are uncorrected and most of them depend on the rate of heating. The infrared spectra were recorded with a Beckman IR-4 spectrophotometer using KBr pellets containing 0.5% by weight of sample, and reported spectra are all calibrated. Ultraviolet spectra were all recorded with a Beckman DK1-A spectrophotometer using 95% ethanol as solvent. Analyses were performed by Micro Tech Laboratories, Skokie, Ill.

2-Isocyanato-4-benzoylcarbamyl Toluene

A solution of 2,4-tolylene diisocyanate (5.0 g, 0.03 mole) and benzoic acid (3.65 g, 0.03 mole) in petroleum ether (100 ml, b.p. 80–100° C) was heated on a steam bath for half an hour. The solution was stirred with a stream of nitrogen to exclude moisture. On cooling of the solution, a compound melting at 84–85° C was obtained which upon crystallizing twice from petroleum ether (b.p. 80–100° C) gave an analytical sample of m.p. 85° C. Yield, 5.8 g (67%). If an excess of benzoic acid was used, the same compound was obtained under the same experimental conditions. Calc. for $C_{16}H_{12}O_4N_2$: C, 64.8%; H, 4.05%. Found: C, 64.8%; H, 4.09%.

2,4-Bis(benzylcarbamyl) Toluene

The dimer of 2,4-tolylene diisocyanate (1.0 g, 0.003 mole) and benzyl alcohol (2 ml) were heated under reflux in petroleum ether (40 ml, b.p. 80–100° C) for 5 hours. The reaction mixture was cooled and the solid filtered, washed with petroleum ether, and dried. The solid was crystallized twice from cellosolve to give an analytical sample of m.p. 217.5° C. Yield, 0.8 g (50%). Ultraviolet absorption spectrum in dimethyl formamide: λ_{max}: 2650 Å, E_{max}: 10,323; inflection point: 2780 Å. The infrared absorption spectrum showed two carbonyl absorption bands of the mixed anhydride at 1775 cm^{-1} (s), 1697 cm^{-1} (s) and C—O—C stretching vibration at 1065 cm^{-1} (s). Calc. for $C_{23}H_{18}O_6N_4$: C, 66.0%; H, 4.30%. Found: C, 66.7%; H, 4.43%.

Attempted Dimerization of 2-Isocyanato-4-methylcarbamyl Toluene

A solution of 2-isocyanato-4-methylcarbamyl toluene (2.0 g, 0.009 mole) in pyridine (10 ml) was kept at room temperature for 24 to 240 hours. No dimer was obtained. A drop of triethyl phosphate as catalyst at elevated temperature (80–100° C) did not give any dimer either.

1,3-Bis(4-methyl-3-n-butyl-carbamylphenyl)-2,4-bis(N-formamido) Uretidine (I)

To a stirred solution of ammonium formate (3.0 g) in ethanol (30 ml), 1,3-bis(4-methyl-3-*n*-butylcarbamylphenyl) uretidine-2,4-dione (1.0 g), m.p. 197°, was added. The mixture was refluxed for 2 hours with constant stirring. The clear solution obtained on vacuum evaporation and dilution gave a precipitate, which was filtered and washed with water. Yield, 0.8 g; m.p. 160–162°. Two crystallizations from ethanol gave the analytical sample with a melting point of 164–165°, molecular weight (Rast) 525. λ_{max}: 2250 Å, E_{max}: 8310. Free NH stretching modes, 3410 cm^{-1} (m), 3050 cm^{-1} (w); amide I band, 1720 cm^{-1} (s); amide II band, 1662 cm^{-1} (m). Calc. for $C_{28}H_{38}O_6N_6$: C, 60.6%; H, 6.85%; N, 15.1%. Found: C, 60.5%; H, 6.62%; N, 14.9%.

N-(4-Methyl-3-n-butyl-carbamylphenyl) Urea (II)

To a solution of 1,2-bis(4-methyl-3-*n*-butyl-carbamylphenyl) uretidine-2,4-dione (1.0 g), m.p. 197°, in 95% ethanol (30 ml) was added hydrazine hydrate (85%, 5 ml). After the reaction mixture was refluxed for half an hour with constant stirring, alcohol (20 ml) was removed *in vacuo*. The residue on cooling gave a compound melting at 201–202°. Yield, 0.7 g. Three crystallizations from acetonitrile gave a pure compound of m.p. 208–209°. λ_{max}: 2830 Å, E_{max}: 13,515; λ_{max}: 2400 Å, E_{max}: 11,130; λ_{max}: 2180 Å, E_{max}: 1325. CO and NH absorptions of the monosubstituted ureas are 1692 cm^{-1} (s), 1610 cm^{-1} (s) respectively. Calc. for $C_{13}H_{19}O_3N_3$: C, 58.8%; H, 7.16%; N, 15.8%. Found: C, 58.7%; H, 6.88%; N, 16.0%.

N,N'-Di(4-methyl-3-n-butyl-carbamylphenyl) Urea (III)

To a stirred suspension of 1,3-bis(4-methyl-3-*n*-butyl-carbamylphenyl) uretidine-2,4-dione (2.0 g), m.p. 197°, in absolute methanol (50 ml), magnesium turnings (1.0 g) were added in small portions while temperature was maintained at 60° for 40 minutes. The reaction mixture was filtered through glass wool and evaporated under reduced pressure. Hydrochloric acid (10%, 50 ml) was then added and the mixture warmed, cooled, filtered, and washed free from acid with water. Crystallization from ethanol–water gave the compound of m.p. 180–181°. Yield 1.6 g. λ_{max}: 2180 Å. E_{max}: 35,720; λ_{max}: 2590 Å, E_{max}: 38,070; inflection point: 2950 Å. CO and NH absorption for disubstituted urea partial structure, 1630 cm^{-1} (m), 1602 cm^{-1} (m) respectively. Calc. for $C_{25}H_{34}O_5N_4$: C, 63.8%; H, 7.23%; N, 11.9%. Found: C, 63.5%; H, 7.23%; N, 12.1%. Reduction with sodium and methanol or with hydrazine hydrate plus 5% solution of sodium in methanol gave the above compound in identical yield. Alkaline reduction with ammonium sulphide at 60° for 4 hours or by zinc and alcoholic ammonia likewise gave the same compound in excellent yields of 80–90%. Mixed melting point determinations showed no depression and the infrared spectra were superimposable.

N-(4-Methyl-3-n-butyl-carbamylphenyl) Formamide Oxime (IV)

To a suspension of 1,3-bis(4-methyl-3-*n*-butyl-carbamylphenyl) uretidine-2,4-dione (m.p. 197°, 1.0 g) in a mixture of ethanol (25 ml) and water (25 ml), hydroxylamine hydrochloride (2.5 g) and sodium acetate (4.0 g) were added, and the reaction mixture refluxed with stirring for 1 hour. After the reaction mixture was evaporated to 30 ml and cooled, a precipitate was obtained, m.p. 169–170° C. Yield, 0.40 g. Two crystallizations from acetonitrile gave the analytical sample of m.p. 170–171°. λ_{max}: 2850 Å, E_{max}: 2630; λ_{max}: 2400 Å, E_{max}: 23,670; λ_{max}: 2180 Å, E_{max}: 31,560. C—N absorption of oxime, 1660 cm^{-1} (s). Free OH stretching frequencies for N—OH group, 3460 cm^{-1} (s) and 3400 cm^{-1} (s). Calc. for $C_{13}H_{19}O_3N_3$: C, 58.8%; H, 7.16%; N, 15.9%. Found: C, 58.7%; H, 7.0%; N, 16.4%.

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